THE ORTHO-ALLYLBENZYL RADICAL: A SENSITIVE PROCEDURE FOR THE ASSESSMENT OF HYDROGEN DONOR SOLVENT REACTIVITY.*

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The thermal conversion of coal involves the decomposition of inter-connected hydroaromatic structures into resonance stabilized benzylic radical fragments. Capping of these radicals with hydrogen from a donor solvent leads to the formation in high yields of lower molecular weight soluble and   volatile products (1-5). In the absence of a donor solvent, the radicals abstract hydrogen from alkyl coal structures and depending on the supply of donatable hydrogen within the coal, conversion yields may be greatly affected (3, 6). In view of the great variety of radicals which must form during coal liquefaction and the many possible competing reactions which lead to products, the ability of a donor solvent to transfer hydrogen to coal radicals is undoubtedly of great importance.

Although much quantitative data describing the reactions of alkyl and heteroatom radicals with hydroaromatic donor solvents exists, (7-9) sur-prisingly little data is available on the reactions of resonance stabilized radicals with hydroaromatic donors (10-14). Realizing the importance of this data to the development of a basic understanding of coal conversion chemistry we have developed a procedure for the quantitative determination of hydrogen donor strengths toward benzyl radical. The method competes the rearrangement of o-allylbenzyl radical against hydrogen transfer to the radical from a donor solvent, see Equations 1 and 2. At this time, the method provides relative and estimated absolute rates of hydrogen atom transfer. Experiments are in progress which are designed to convert these relative rates to absolute rates with a high degree of accuracy and precision.

Experimental

Synthesis of o-allylazotoluene. o-allylbenzylazine was synthesized from o-allylbenzaldehyde and hydrazine sulfate according to the procedure of H. H. Hatt (15). The azine was reduced to its corresponding hydrazine derivative with Na-Hg(5%) in methanol. o-Allylbenzylhydrazine was oxidized to o-allylazotoluene according to the procedure of Cohen and Wang (16); m.p. 47.5-49.0°C; NMR (CDCl$_3$) , 7.33-7.20 (sharp m, 8H, aromatic-H), 6.25-5.75 and 5.15-4.80 (m, 6-H, olefinic-H), 4.96 (s, 4-H, benzyl-H to nitrogen atom, superimposed on vinyl region), 3.48 (d of t, 4-H, J = 6.2, 1.5Hz, benzyl-H to vinyl group); Analyses: Calc., C, 82.72, H, 7.64, N, 9.65; found, C, 82.6, H, 7.73, N, 9.58.
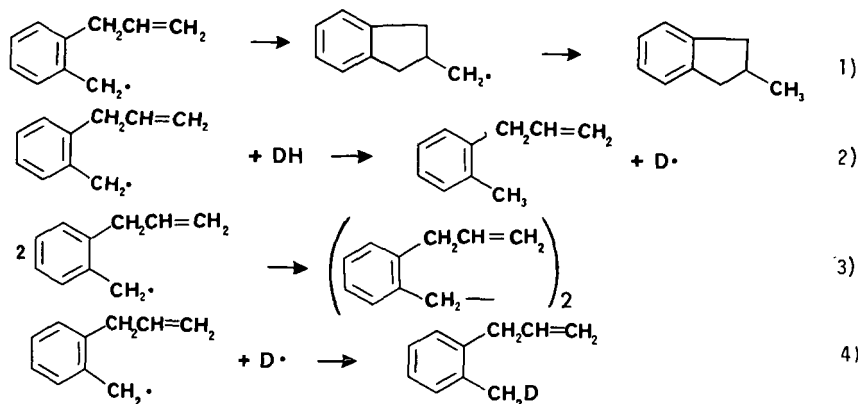
Determination of relative rates of hydrogen atom transfer to o-allylbenzyl radical. Solutions of the o-allylazotoluene, hydrogen donor, and sometimes an inert solvent such as benzene or phenyl ether, were degassed and sealed in pyrex tubes and then thermostatted for 20 minutes (approximately 2 half-lives). The concentration of azo compound was kept low (<.01M) to minimize radical induced decomposition and to minimize consumption of donor solvent (usually <5% consumed). The relative amounts of 2-methylindan (2MI) and

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and o-allyltoluene (OAT) were determined by capillary gas chromatography analysis after they were separated from the unreacted azo compound by high performance liquid chromatography. In calculating k_{abs}/k_{re}, the room temperature concentrations of donor solvents were corrected to reflect the solution density at 160°C (17). We expect the error in these values to be ±5% due to lack of precise information about the actual liquid densities.

Results and Discussion

o-Allyazotoluene is a conviently prepared thermal source of o-allyl-benzyl radicals. In donor solvents equilivant to or better than m-xylene it has a half-life of approximately 10 min at 160°C. Upon decomposition, a pair of o-allylbenzyl radicals form and undergo reactions of rearrangement, hydrogen abstraction and combination.

$$\text{o-allylbenzyl radical} \longrightarrow \text{2-methylindan CH}_2\cdot \longrightarrow \text{2-methylindan CH}_3 \qquad 1)$$

$$\text{o-allylbenzyl radical} + DH \longrightarrow \text{o-allyltoluene} + D\cdot \qquad 2)$$

$$2 \,\text{o-allylbenzyl radical} \longrightarrow \left(\text{dimer} \right)_2 \qquad 3)$$

$$\text{o-allylbenzyl radical} + D\cdot \longrightarrow \text{CH}_2D \text{ product} \qquad 4)$$

The yields of products, 2-methylindan (2MI), and o-allyltoluene (OAT), formed from the competing reactions of rearrangement, Equation 1 and hydrogen atom abstraction, Equation 2, are observed to vary according to the hydrogen donor strength of the donor solvent (DH). Under the experimental conditions, the formation of 2MI and OAT are irreversible and the amount of DH consumed is small, so that the rate constant for hydrogen abstraction, k_{abs}, relative to rearrangement, k_{re}, for a given donor is provided by the expression,

$$\frac{k_{abs}}{k_{re}} = \frac{[OAT]}{[2MI][DH]n} \qquad 5)$$

where n is the number of donatable hydrogens per donor molecule.

The formation of 2MI is controlled by the unimolecular rearrangement of o-allylbenzyl and the rate constant, k_{re}, for this reaction is independent of solvent composition, such that the values, k_{abs}/k_{re}, provide a quantitative index of hydrogen donor strength. In Table I, index values for a series of hydrogen donor solvents and model compounds have been compiled from k_{abs}/k_{re} values. For convience of comparison, the values have been indexed relative to m-xylene for which k_{abs}/k_{re} is 2.53×10^{-3}.

Interestingly the index quantitatively bears out the expected relationship between donor strength and resonance stabilization energy of the radical formed from the donor molecule, i.e., 9,10-dihydroanthracene > allylbenzene > 9,10-dihydrophenanthrene > diphenylmethane > m-xylene. Diphenylmethane is

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a much poorer solvent than dihydroanthracene because steric hinderance prevents both phenyl rings from being simultaneously conjugated with the radical site. Little steric hinderance is in effect for the radical derived from allylbenzene and therefore the radical experiences greater resonance stabilization than diphenylmethyl radical and exhibits a greater rate of hydrogen donation. Of the recyclable solvents, 9,10-dihydroanthracene is a far superior donor to tetralin or 9,10-dihydrophenanthrene.

The index quantitatively illustrates the astonishing effects of combined polar and resonance effects in accelerating atom transfer reactions, i.e., thiophenol > phenol > xylene. These results indicate that compounds such as naphthols and thiols are among the most important donors in high sulfur coals and oxygen rich medium ranked coals. It is clear that they play important and as yet relatively unknown roles in the formation of soluble conversion products and chars (18).

These results easily show the importance of establishing such a method for assessing donor solvent strengths. Furthermore, good methods for estimating the Arrhenius parameters for the absolute rate of rearrangement for o-allylbenzyl radical are at hand (19) and an experimental determination is in progress. Therefore, this body of data will be of great value both to researchers involved in developing thermochemical kinetic models of coal liquefaction and to investigators interested in understanding basic chemical transformations.

Table I. Hydrogen Donor Strength of Selected Solvents and Model Compounds Towards o-Allylbenzyl Radical.

Donor	Relative Donor Strength
m-xylene[a]	1
1,5-Cyclooctadiene	11
Diphenylmethane	20
Tetralin	27
9,10-Dihydrophenanthrene	33
Phenol	76
Allylbenzene	114
9,10-Dihydroanthracene	635
Tri-n-butylstannane	3.2×10^5
1-Naphthol	1970
Thiophenol	1.10×10^6

[a] $k_{abs}/k_{cyc} = 2.53 \times 10^{-3}$

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